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PHASE I

ORGANICS IN WATER CONTAMINATION ANALYZER

FINAL REPORT

June 2, 1986

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HOUSTON, TEXAS

IONICS RESEARCH, INC., 22 SANDALWOOD DRIVE

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ALBERT ZLATKIS, PRESIDENT

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ORGANICS IN WATER CONTAMINATION ANALYZER

ABSTRACT

This study was undertaken to define the requirements which would result in identifying the components of an automatic analytical system for the analysis of specific organic compounds in the Spacestation potable water supply. The gas chromatographic system for such an analysis is limited to commercially available off-the-shelf hardware and includes the sample inlet, an ionization detector, capillary columns as well as computerized compound identification. The sampling system will be a special variation of the purge and trap Tenax mode using six-port valves and a 500 microliter water sample. Capillary columns used for the separating of contaminants will be bonded phase fused silica with a silicone stationary phase. Two detectors can be used: (a) photoionization and (b) far ultraviolet since they are sensitive and compatible with capillary columns. A computer system evaluation and program with the principle of compound identification based on the retention index is presented.

OBJECTIVES

Phase I of this program is concerned with a study of state-of-the art technology and selection of off-the-shelf hardware that will result in analytical instrumentation for the determination of organic contaminants in water. Such an instrument should with few system modifications result in a qualifiable flight gas chromatograph for the analysis of the Spacestation potable water supply.

GAS CHROMATOGRAPHIC DETECTORS

The 38 components of representative compounds listed in Attachment 1 are best separated and analyzed by gas chromatography. The gas chromatograph with which we have the most experience is the Hewlett-Packard, Model 5890, an instrument compatible with capillary columns. The ionization detectors considered in this study were: (1) Photoionization detector and (2) Far ultraviolet detector.

(1) Photoionization detector

This detector operates on the principle of ionizing the organic compounds emerging from the column by using photons produced in a discharge in argon or helium. The commercially available detector (HNU Systems Inc., 160 Charlemont St., Newton, MA 02161) uses a discharge lamp containing a mixture of gases at low pressures which are excited by a high voltage across two electrodes in the evacuated chamber. UV sources are available at different energies to effect selectivity. The low detector volume of 150 microliters permits the use of capillary columns. This detector does not destroy the sample, requires only one gas (carrier) and is easy to operate. It is more sensitive than the flame ionization detector and does not respond to air or water.

(2) Far Ultraviolet Detector

This detector makes use of a new photodiode, stable UV lamps and measures absorbance at 120 nm. Since it has a universal response except for the noble gases, the latter can be used as carrier gases. The small detector volume of 40 microliters allows the use of capillary columns. Further, the sensitivity of this detector is enhanced by using low flow rates demanded by capillary columns, since it is concentration dependent.

Other detectors such as the argon ionization, helium ionization and flame ionization are somewhat limited for the Spacestation. The argon ionization detector is not commercially available, the helium ionization detector is difficult to use because of the requirement of keeping any environmental contaminants out of the system and the flame ionization detector requires the use of three gases and the presence of a flame. The Photoionization detector manufactured by HNU Systems, Inc. appears to be the detector of choice at present since the Far UV detector has just become commercially available.

COLUMN TECHNOLOGY

The gas chromatographic columns to be used in the system should have the following characteristics:

- (a) column material must be fused silica in order to have a minimum of adsorption sites.
- (b) stationary phase should be bonded - this will give greater thermal stability. Large volumes of water due to multiple sampling will not affect the longevity of an apolar column.
- (c) capillary dimensions to yield high efficiency and resolution - this is required to separate and quantitate the compounds in the SOW.
- (d) capability of interfacing with a mass spectrometer if so required.
- (e) capability of being used with detector of choice.

Such columns are available commercially in lengths up to 50 meters, I.D.'s of 0.2 - 0.53 mm and film thickness of 0.1 - 5 microns. A number of apolar and polar stationary bonded (polymethylsiloxane, polymethylphenylsiloxane and carbowax 20M) phases can also be obtained readily. The following companies are sources for the capillary fused silica columns:

J & W Scientific, Inc.	Rancho Cordova, CA
Quadrex Corp.	Woodbridge, CT
Hewlett-Packard	Avondale, PA
Foxboro Analabs	North Haven, CT

SAMPLE INLET SYSTEM

The proposed introduction and analysis of samples will involve

a purge and trap Tenax system. 500 microliters of the water sample will be introduced with purified air being used as both purge and carrier gas. The six-port HPLC valves are commercially available from Valco Instruments Co. in Houston, TX.

SAMPLING SYSTEMS

SYSTEM A

Sampling Purge Phase (cold Tenax) Figure 1.

1. An exactly sampled amount of water (500 μ l) is filled into container 8. It should be noted that 0.01% sample volume precision presents no problem, however, such requirements at the ppm and ppb level are not necessary because all other unavoidable errors are two orders of magnitude less precise.
2. Carrier gas air which is chromatographically clean is used to extract all of the compounds in 15 - 20 minutes by bubbling through containers 8 and 9. The enriched gas passes through precolumn 10 and a split at 10 allows for a full flow transfer. Item 10 is a Tenax precolumn and valve 11 is open during the Tenax "cold" phase of 4°C.
3. Air continues to backflush the water sample container 8 and to forward flush the precolumn 10 (now at high temperature) into the temperature programmed parallel double capillary GC system. Parallel detectors of different types feed two data channels; one is used for quantitation and both are used in calculating the signal ratio to confirm identification. The time difference from both channels is used to produce the retention index increment data, thereby producing a qualitative/quantitative report. Because full extraction is not possible, it will be necessary to run calibrations with the listed compounds in prior laboratory tests. About 25% of these compounds will be transferred by the air in 15 minutes and can be measured at the sub ppb range for all compounds except the alcohols. A full analysis is possible every 60 minutes. A simple multi channel timer will control about 5 switches, two of which will be used to rotate two 6-port valves (Valco HPLC valves).

Analysis Phase

1. The analytical data are taken from a double channel total digitization device producing two raw data sets of 2048 raw

data points each. The precision retention time data are taken from polynomial raw data interpolation around the peak maxima offering 0.01 second data precision. POSTRUN programs take the raw data for integration, retention time interpolation, retention index (RI) and RI-increment calculation as well as signal ratio calculation. The whole data processing is automatic but discontinuous. Each run is started by the temperature change command at precolumn 10.

2. The hardware used will be two ADALABS on-line Apple IIe or IIc. The software used is Appleworks, IfC-LEK Auto-videogratiion and IfC Polynomial Retention Index interpolation. The long range result analysis is based on Appleworks database comparison (manual interaction only). Datafiles for the database part of Appleworks will be produced automatically and the REPORT per analysis will be stored on disk and/or immediately printed out. No decision has been made regarding the printer since we do not know of any light weight quality printer with graphics and stability comparable to the Epson FX 80.
3. A double drive Apple IIc will be used. However, an Apple IIe would be better as it can be more easily upgraded with 1.2 megabyte extra RAM and everything which has been summarized above is already working on the IIe, but not yet on the IIc.

SYSTEM B

The principal difference of A versus B is that there is an absolute analysis in the latter. Precolumn 19 is backflushed by a liquid; here, the water sample is partially evaporated and completely extracted in 19. This proposed procedure will require intensive experimentation before further consideration.

1. 500 μ l water sample is passed through 18. During this period 19 is backflushed and cleaned. The water sample is passed onto the cold precolumn and most of the water is flushed out by chromatographically clean air.
2. The now wet precolumn is forward flushed into a double column, double channel chromatographic system and the precolumn is heated. It should be possible to trap all compounds from methanol through the last eluting one, but with quite a large water load. The precolumn packing should be Tenax.
3. Data analysis as in SYSTEM A.

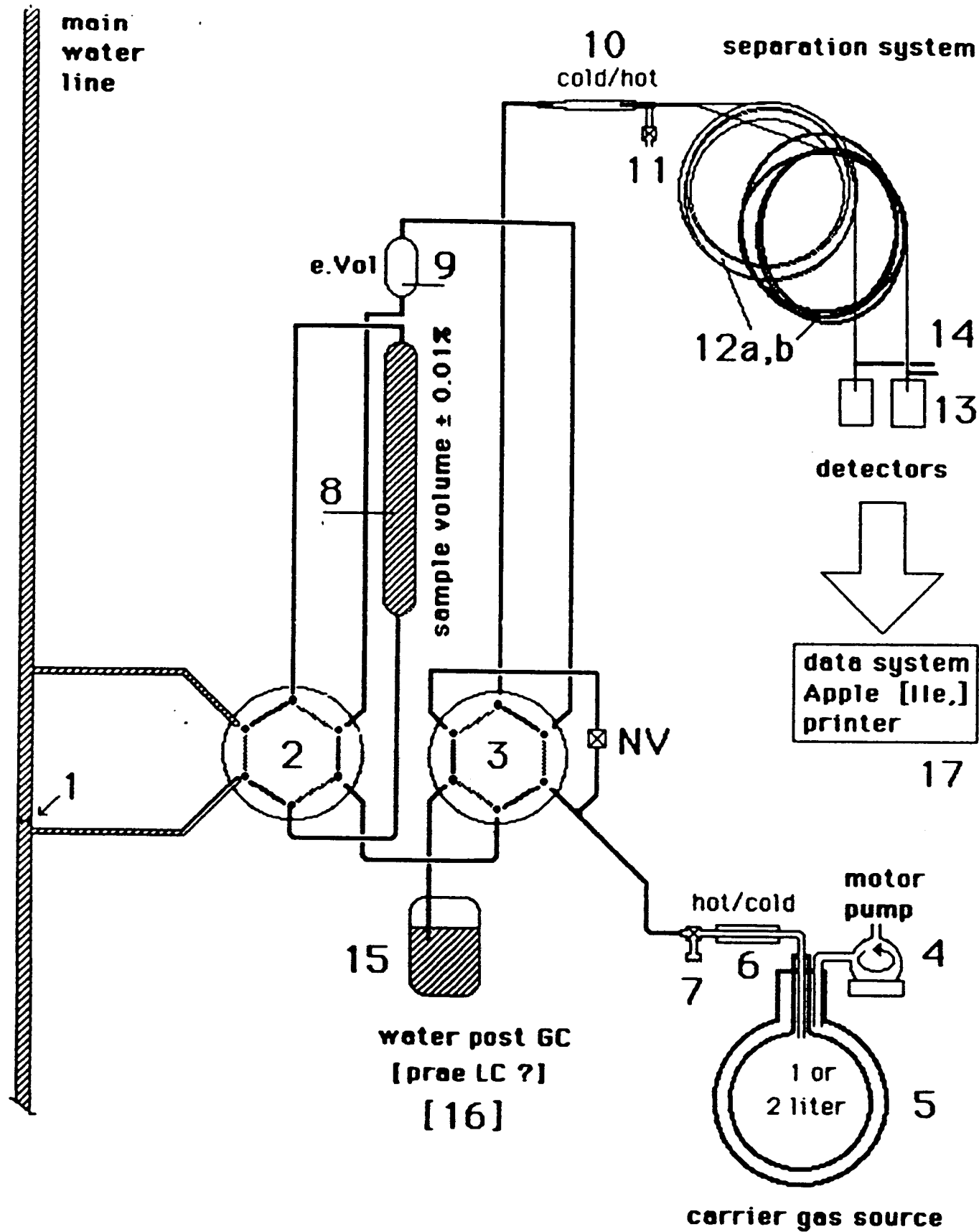


Figure 1

COMPUTER SYSTEM EVALUATION AND PROGRAM

The following text is partially written in an abbreviated form similar to a computer language. The commands underlined represent Basic commands as well as Subprograms which are named labels and can be placed anywhere in a program.

The software package is written in ZBasic and runs device independent on a variety of computers including Apple IIe, IIc and Macintosh. ZBasic can be written completely in unnumbered subprograms, which allows the utmost flexibility - quite similar to FORTH, but more powerful, especially with respect to the mathematics involved. Using the retention index as the principle of qualitative chromatographic analysis it was found, that a mathematical accuracy of more than 16 - optimal 22 digits are necessary to make full use of chromatographic time data precision available (and necessary in double channel high speed separations) at a level of 0.01 seconds.

ZBasic allows us to configure an Apple IIc for 54 digits double precision mathematics or a Macintosh to 240 digits double precision mathematics (not needed for chromatography). ZBasic runs, when compiled, are quite fast on Macintosh, IBM PCAT and similar 16/32 bit micros. The speed of compiled ZBasic on an Apple IIc is high enough for the task described in the following part. The final ZBasic program was compiled and requires 64 K RAM machines only but runs on 128 K RAM and higher memory enhanced computers. It is assumed that we have a chromatograph running which produces a two channel chromatogram simultaneously similar to figure 2:

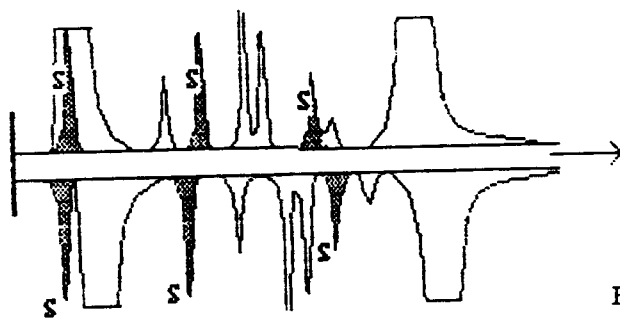


Fig. 2

"S" in the figure above represents known or added qualitative inner standards belonging to a homologous series. Both chromatogram

channels differ in polarity but have separated the same sample, injected simultaneously into both columns, which are fed by carrier gas pressure from exactly the same carrier gas source. The chromatograms are artificial. A true picture looks much more complex, but this does not change in the software principle described below.

This principle of compound identification based upon the Retention Index and the retention index increment is given in the following word program:

```
START GC sampling, separation, raw data collection.  
  STORE raw data (a set of up to 2048 12 bit signal  
    Height slices taken at precise and constant time  
    intervals). The raw data slices provides  
    very accurate Time information.
```

After end of run

```
INTEGRATE raw data,  
  find RETENTION TIME/PEAK HEIGHT/AREA,  
STORE T(1...N), H(1...N), A(1...N) for N peaks  
  
START DATA TREATMENT  
  IF isothermal GOSUB DEAD TIME calculation  
  GOTO REFERENCE (completes the integrated data  
    sets with reference index data).  
  IF isothermal GOSUB ISOTHERMAL INDEX calculation:  
  GOTO INDEX TABLE  
  GOTO TGC INDEX calculation: GOTO INDEX TABLE  
  
INDEX TABLE: CHECK ERROR: ON ERROR GOTO ALARM (1...X)  
  
PRINT REPORT  
  GOSUB DECISION TABLE:GOTO START GC .
```

The following subprogram units are in practical long term application:

```
START GC  
STORE  
INTEGRATE  
RETENTION TIME/PEAK HEIGHT/AREA  
STORE  
DEAD TIME  
ISOTHERMAL INDEX
```

TGC INDEX
REPORT

For continuation of any further programming we need exact orders about the details of REFERENCE, INDEX TABLE, ALARM (1...X), and the DECISION TABLE.

Questions:

- Which columns will be used?
- Isothermal or temperature programmed or combined runs?
- How will the referenced compounds be added to the sample, which must include all substances to be Index-checked?
- Which reference compounds will be used?
- Which compounds MUST, which SHOULD, which could be compiled into the INDEX TABLE:
- Which Alarm (1...X) actions are planned?
- Which decisions are to be made upon analytical results in quantitative and qualitative aspects?
- Which system will digitize the chromatogram signal?
- How and where will the raw data be stored? We would not recommend using the drives.

The latest information send in April 1986 by I. M. Inc. State College (the producer of ADALAB) is terminating production of a qualified ADALAB which can run in any computer. Only ADALABS is available which can run in an Apple IIe or an IBM PCat. There are no more plans to offer SERIAL PORT (RS232) ADALABS. 16 bit AD-serial RS232 system for chromatography can now be obtained from the Institute of Chromatography, Bad Durkheim, Germany. The Apple IIc 28 volt DC power adapter runs at 30 to 22 volt levels without any heating-up problems.

ATTACHMENT 1
REPRESENTATIVE COMPOUNDS

ALCOHOLS

Methanol
n-Butanol
n-Propanol
Isobutanol
Isopropanol

ALDEHYDES

Acetaldehyde
Acrolein
Butyraldehyde
Propionaldehyde

ALIPHATICS

1,3-Butadiene
1-Butene
Isoprene

AROMATICS

Ethylbenzene
Mesitylene
n-Propylbenzene
Styrene
m-Xylene
Benzene
Toluene

ESTERS

Butylacetate
Ethylacetate
Isobutylacetate
n-Propylacetate

HALOCARBONS

Carbon Tetrachloride
Chlorobenzene
Dichlorobenzene
Methylchloride
Methylchloroform
Tetrachloroethylene
Trichloroethylene
Vinylidene Chloride
1,2-Dichloroethane
Dichlorofluoromethane
Methyl Chloride

HETEROCYCLICS

1,4-Dioxane
Tetrahydrofuran

KETONES

Methylethyl Ketone
Methylisobutyl Ketone